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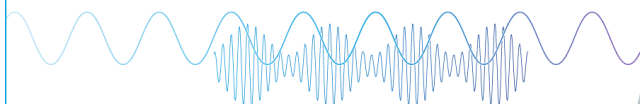
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# Vapor deposition rate modifies anisotropic glassy structure of an anthracene-based organic semiconductor

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## ABSTRACT

We control the anisotropic molecular packing of vapor-deposited glasses of ABH113, a deuterated anthracene derivative with promise for future organic light emitting diode materials, by changing the deposition rate and substrate temperature at which they are prepared. We find that at substrate temperatures from 0.65  $T_g$  to 0.92  $T_g$ , the deposition rate significantly modifies the orientational order in the vapor-deposited glasses as characterized by x-ray scattering and birefringence. Both measures of anisotropic order can be described by a single deposition rate–substrate temperature superposition (RTS). This supports the applicability of the surface equilibration mechanism and generalizes the RTS principle from previous model systems with liquid crystalline order to non-mesogenic organic semiconductors. We find that vapor-deposited glasses of ABH113 have significantly enhanced density and thermal stability compared to their counterparts prepared by liquid-cooling. For organic semiconductors, the results of this study provide an efficient guide for using the deposition rate to prepare stable glasses with controlled molecular packing.

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## INTRODUCTION

Organic light emitting diodes (OLEDs), first discovered in 1987,<sup>1</sup> are ubiquitous in current electronic display technologies.<sup>2–4</sup> The rapidly growing worldwide OLED industry is currently valued at USD  $38 \times 10^9$  and is projected to reach USD  $73 \times 10^9$  by 2026.<sup>5</sup> As the roughly 30-year industry matures, novel uses, such as in biomedical devices<sup>6</sup> and automotive lighting, continue to expand the industry. Since OLED technologies are so widespread and frequently used, improvements in critical device parameters, such as stability, energy efficiency, and device lifetime, can have a significant impact on worldwide energy and resource use.

OLED devices have been extensively optimized by chemically modifying the organic semiconductors used to transport charges.<sup>7</sup> Anthracene derivatives are one type of molecule commonly used for OLEDs. These molecules have good electroluminescence, photoluminescence, and electrochemical properties due to their rigid ring structure and 14  $\pi$ -electron aromaticity.<sup>8–13</sup> While some anthracenes are prone to crystallization, chemical modification is readily achieved, and the proper choice of substituents can

suppress crystallization while minimally impacting (or even improving) the electronic properties.<sup>14,15</sup> The use of deuterium-substituted molecules is also an important strategy to improve chemical stability and increase emitter efficiency. The chemical stability of the molecules used in OLEDs is important for maximizing the lifetime of the devices, and replacing the C–H bonds in the molecules with less labile C–D bonds inhibits degradation.<sup>16</sup> This is a general design mechanism that does not depend upon whether deuterium substitution is directly on aromatic rings or in other parts of the molecule. Deuterium substitution in fused aromatic systems is also beneficial as this can increase the emitter lifetime by decreasing the excited state decay constant.<sup>17,18</sup> For example, deuterium substitution in emitter complexes such as Ir(ppy)<sub>3</sub> and Alq<sub>3</sub> has been shown to increase current density, external quantum efficiency, and device lifetime.<sup>19,20</sup>

OLEDs are typically prepared by physical vapor deposition (PVD) in vacuum, and a second approach to optimizing OLED performance is to control the anisotropic structure of the glass prepared by deposition.<sup>21</sup> In the PVD process, molecules are condensed in vacuum onto a temperature-controlled substrate at a

controlled deposition rate. The glasses prepared by this method are often anisotropic,<sup>21–24</sup> and according to the surface equilibration mechanism, this is a consequence of the high mobility of organic glass surfaces.<sup>24,25</sup> During vapor deposition, enhanced mobility at the surface of the glass allows the molecules to partially equilibrate toward the preferred surface structure (which is generally anisotropic) before becoming locked into the bulk by further deposition. The anisotropic packing of these glasses can enhance efficiency by improving charge mobility and directional emission.<sup>26</sup> Glasses prepared by this method can homogeneously incorporate multiple components with controllable molecular orientation, which is important for the host-emitter layers that are used in OLEDs.<sup>22,27</sup> The increased mobility at the free surface has also been shown to prepare glasses with enhanced thermal and kinetic stability,<sup>25,28</sup> which, in turn, increases OLED lifetimes.<sup>29</sup>

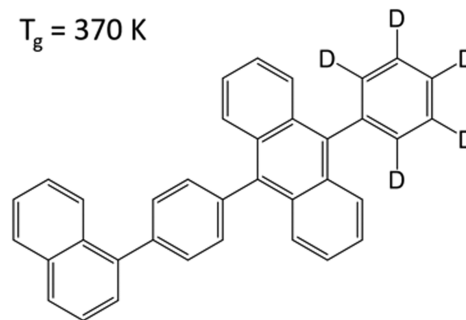
The effects of deposition rate and substrate temperature upon the anisotropic structure of PVD glasses can be related quantitatively using “deposition rate–substrate temperature superposition” or RTS. During a typical deposition, molecules at the surface are kinetically trapped by further deposition before they completely equilibrate to the preferred surface structure. Further equilibration during deposition can be achieved either by depositing more slowly or by depositing at a higher temperature. When RTS describes the data, the implication is that adjusting the deposition rate and the substrate temperature are equivalent paths to producing a particular structure. We have previously reported that RTS works for systems forming glasses with liquid-crystal-like packing.<sup>30–32</sup> OLED systems have also been deposited at various rates and  $T_{\text{sub}}$ , and both variables modify the anisotropic structure, although so far RTS has not been tested over a wide range of rates and substrate temperatures.<sup>23,33</sup> RTS is practically important as it reduces a two-dimensional parameter space to a single variable. Conceptually, demonstration of RTS supports the applicability of the surface equilibration mechanism.

In this work, we show that the anisotropic structure and molecular packing in stable glasses of ABH113, a deuterium-substituted anthracene derivative, can be successfully described by the RTS principle. We vapor-deposit glasses over a wide range of substrate temperatures ( $T_{\text{sub}} = 0.65\text{--}0.92 T_g$ , where  $T_g$  is the glass transition temperature) and deposition rates ( $0.1\text{--}10 \text{ \AA s}^{-1}$ ) to modify the anisotropic molecular packing. We find that the glasses prepared at these conditions have enhanced thermal stability and greater density, relative to liquid-cooled glasses. We characterize the anisotropic order in the deposited glasses by spectroscopic ellipsometry and grazing-incidence x-ray scattering and find that the two measures of structure are described by the same scaling behavior as a function of rate and temperature. The deposition rate and substrate temperature can be quantitatively related by RTS. These results indicate that we can successfully control and predict anisotropic glassy packing over a wide range of conditions for a typical OLED material.

## MATERIALS AND METHODS

### Material characterization

ABH113 (SFC Co., Ltd., South Korea) was used as-received. The structure of ABH113 is shown in Fig. 1. The glass transition temperature  $T_g$  was determined by differential scanning calorimetry (DSC, TA Instruments Q100) at scanning rates of 5 K/min, as shown



**FIG. 1.** Molecular structure of ABH113, a deuterated anthracene derivative.  $T_g$  is determined by DSC (see the [supplementary material](#)) and ellipsometry (shown in Fig. 7).

in Fig. 1 of the [supplementary material](#). Briefly, the as-received crystalline powder was heated to 523 K, showing an endothermic melting peak at 500 K. The sample was cooled with no apparent crystallization, and the onset of the glass transition was measured during the sample's second heating to be  $T_g = 370 \text{ K}$ . *In situ* ellipsometry thickness measurements on vapor-deposited ABH113, shown in Fig. 7, are consistent with the  $T_g$  determined by DSC.

### Vapor deposition

Glasses were vapor-deposited in a custom-built deposition chamber as detailed in previous publications,<sup>24</sup> utilizing a source-to-substrate distance of 11 cm and a base pressure of  $\sim 10^{-7}$  Torr. 1-in. Si (100) wafers (Virginia Semiconductor) were affixed to copper fingers using Apiezon Grease N ( $T_{\text{sub}} < 293 \text{ K}$ ) or Apiezon Grease H ( $T_{\text{sub}} \geq 293 \text{ K}$ ). The copper fingers were cooled using liquid nitrogen, and Lakeshore 336 and 340 instruments were used to control heaters to achieve the desired substrate temperature. A quartz crystal microbalance (Sycon Instruments) was used to monitor deposition rate *in situ*. Films were 100–250 nm thick, as characterized by ellipsometry.

### Ellipsometry measurements

The as-deposited glasses were measured at 21 locations on each 1-in. wafer using an M-2000U spectroscopic ellipsometer from Woollam Co., Inc. Each location was measured at seven incident angles from  $45^\circ$  to  $75^\circ$  in increments of  $5^\circ$ . In order to minimize errors, the ellipsometry beam was perpendicular to the sample thickness gradient (caused by the deposition geometry). Data collected at wavelengths from 500–1000 nm were modeled using a uniaxially anisotropic Cauchy model,

$$n_z = A_z + \frac{B}{\lambda^2}, \quad n_{xy} = A_{xy} + \frac{B}{\lambda^2},$$

with the  $z$  direction defined as normal to the substrate. The  $x$ - and  $y$ -directions are in-plane and equivalent, i.e., the PVD glasses exhibit uniaxial anisotropy. The birefringence  $\Delta n$  is equal to  $n_z - n_{xy}$ , or  $A_z - A_{xy}$ , at 632 nm. Error bars shown in Figs. 5 and 6 are the standard deviations of birefringence values measured at all positions of a wafer.

## X-ray scattering

Grazing-incidence wide-angle x-ray scattering (GIWAXS) was performed at Beamline 11-3 of the Stanford Synchrotron Radiation Laboratory (SSRL) using a source-to-detector distance of 315 mm with 12.7 keV x rays ( $\lambda = 0.976 \text{ \AA}$ ). All data shown were taken at an incidence angle of  $\theta = 0.12^\circ$ . The orientational order parameter  $S_{\text{GIWAXS}}$  is defined as in Eq. (1),

$$S_{\text{GIWAXS}} = \frac{1}{2}(3\langle \cos^2 \chi \rangle - 1), \quad (1)$$

where  $\chi$  is the azimuthal angle in reciprocal space with  $\chi = 0^\circ$  defined along  $q_z$ . The  $\langle \cos^2 \chi \rangle$  average of the scattering intensity between  $q$  values of 1.1 and  $1.7 \text{ \AA}^{-1}$  is defined in Eq. (2),

$$\langle \cos^2 \chi \rangle = \frac{\int_0^{90} I(\chi)(\cos^2 \chi)(\sin \chi) d\chi}{\int_0^{90} I(\chi)(\sin \chi) d\chi}, \quad (2)$$

and is taken after an empirical B-spline background subtraction and subsequent extrapolation to all azimuthal angles, as used in previous publications<sup>32</sup> and shown in Figs. 2 and 3 of the [supplementary material](#).

## Liquid-cooled and spin-coated glass preparation

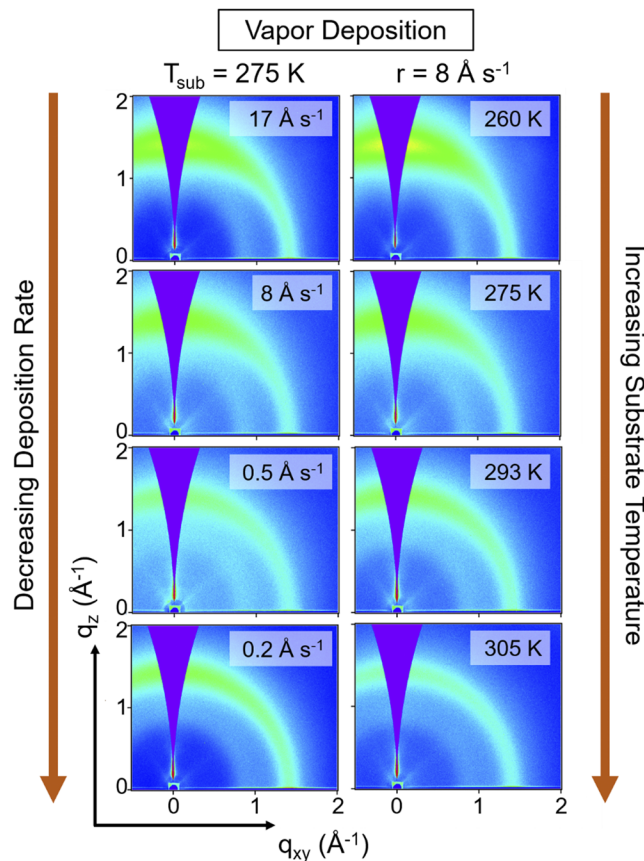
Two reference samples were prepared for comparison with PVD glasses. One reference sample was spin-coated on a 1-in. Si wafer treated by uv/ozone cleaning. A 1.5 wt. % solution of ABH113 in cyclohexanone was spin coated at 2100 rpm for 30 s. The sample was then baked in a nitrogen atmosphere at  $80^\circ\text{C}$  for 2 min. This sample was 90 nm thick. As a second reference sample, a liquid-cooled glass was prepared by vapor deposition at 400 K ( $T_g + 30 \text{ K}$ ), followed by cooling at  $2 \text{ K/min}$ .

## RESULTS

### Structure of PVD glasses of ABH113

When deposited at various substrate temperatures ( $T_{\text{sub}}$ ) and deposition rates, ABH113 forms glasses with a range of anisotropic packing arrangements, as shown in Fig. 2. The main feature in all scattering patterns is an amorphous halo at  $q \approx 1.4 \text{ \AA}^{-1}$ . This corresponds to a real-space periodicity of  $\approx 4.5 \text{ \AA}$ , which we interpret as the average interaction length between two neighboring molecules. While the scattering intensity at  $q \approx 1.4 \text{ \AA}^{-1}$  occurs at all azimuthal scattering angles  $\chi$ , the scattering intensity is greater along  $q_z$  for most deposition conditions, indicating anisotropic molecular packing.

When deposited at a constant  $T_{\text{sub}}$ , depositing more slowly resulted in a more isotropic distribution of scattering of the amorphous halo. The left column of Fig. 2 shows a subset of samples prepared at a constant  $T_{\text{sub}}$  of 275 K. At the highest deposition rate of  $16 \text{ \AA s}^{-1}$  (top left panel), the scattering is focused along  $q_z$ , indicating nearest-neighbor interactions that occur primarily out-of-plane of the film. As the deposition rate is decreased, the out-of-plane scattering decreases, and at the lowest deposition rate of  $0.16 \text{ \AA s}^{-1}$  (bottom left panel), the scattering at  $q \approx 1.4 \text{ \AA}^{-1}$  is nearly equal at all scattering angles.



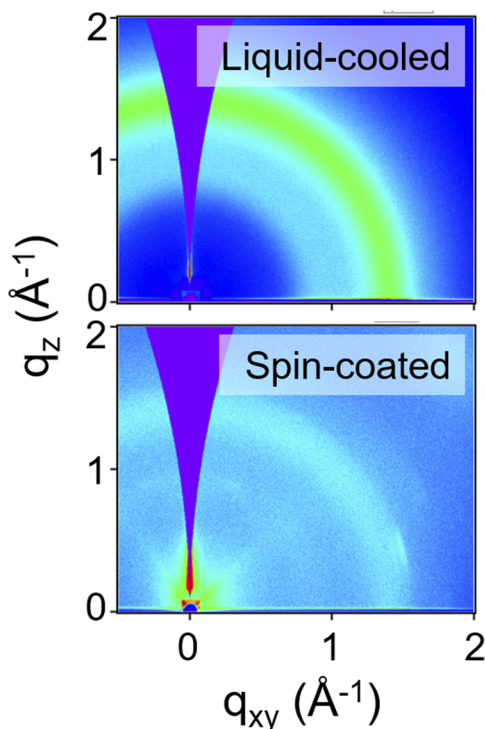
**FIG. 2.** Grazing-incidence wide-angle x-ray scattering (GIWAXS) patterns of vapor-deposited glasses of ABH113. Left: glasses prepared at four deposition rates at a constant  $T_{\text{sub}}$  of 275 K. Right: glasses prepared at four substrate temperatures at a constant rate of  $\sim 10^{0.9} \text{ \AA s}^{-1}$ . Note that the images in the second row of both columns of the figure are the same sample, providing a convenient frame of reference between the two control parameters.

When deposited at a constant rate of  $8 \text{ \AA s}^{-1}$ , increasing  $T_{\text{sub}}$  similarly makes the scattering more isotropic, as seen in the right column of Fig. 2. At this deposition rate, the sample deposited at the lowest  $T_{\text{sub}}$  (upper right panel) has scattering focused primarily out-of-plane. As the  $T_{\text{sub}}$  of deposition is increased toward 305 K (bottom right panel), the scattering becomes isotropic at all scattering angles  $\chi$ .

In Fig. 2, we see that decreasing the deposition rate and increasing  $T_{\text{sub}}$  have the same qualitative effect upon the anisotropic glass structure of vapor-deposited ABH113. For both parameters, more isotropic glasses are obtained when deposited at a decreased deposition rate or an increased substrate temperature. This suggests that at these conditions, molecules can more fully equilibrate at the free surface during deposition.

The PVD glasses of ABH113 prepared here are distinct from those that can be prepared by conventional methods. Figure 3 shows the x-ray scattering from glasses prepared by liquid-cooling and spin-coating. For the liquid-cooled sample, the amorphous scattering peak at  $q \approx 1.4 \text{ \AA}^{-1}$  is completely isotropic, with



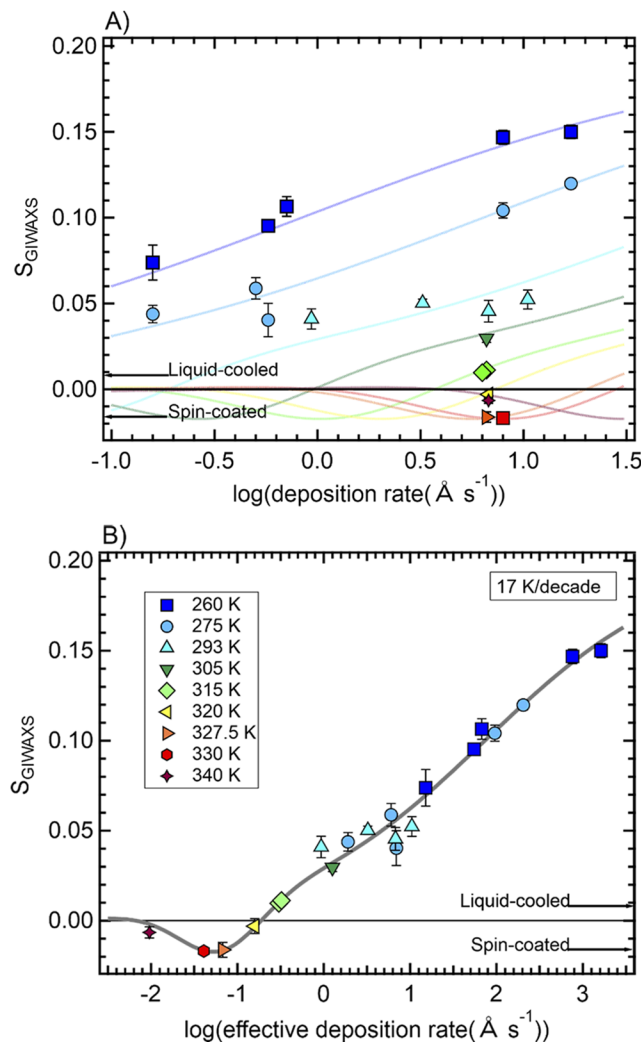


**FIG. 3.** ABH113 glasses prepared by cooling from the equilibrium liquid and by spin-coating. For both reference glasses, scattering near  $q \approx 1.4 \text{ \AA}^{-1}$  is nearly isotropic.

equal scattering intensity at all azimuthal angles. It closely resembles the scattering patterns from the glasses vapor-deposited at the highest  $T_{\text{sub}}$  and lowest rates. The spin-coated sample shows weaker scattering, although the major scattering feature is similarly isotropic. In addition, the spin-coated sample shows minor scattering features (at  $q \approx 1.5 \text{ \AA}^{-1}$  and  $\chi \approx 70^\circ$ ) whose origin is unknown.

### Test of rate-temperature superposition

The anisotropy of the x-ray scattering near  $q \approx 1.4 \text{ \AA}^{-1}$  can be quantified using the Hermans orientation order parameter,  $S_{\text{GIWAXS}}$ .<sup>34,35</sup> A value of  $S_{\text{GIWAXS}} = +1.0$  corresponds to scattering focused entirely out-of-plane, while an  $S_{\text{GIWAXS}} = -0.5$  corresponds to scattering completely in-plane (along  $q_{xy}$ ). A glass with isotropic scattering will have an  $S_{\text{GIWAXS}}$  of 0. Figure 4(a) shows how  $S_{\text{GIWAXS}}$  varies as a function of the log of the deposition rate for several  $T_{\text{sub}}$  values. At each substrate temperature,  $S_{\text{GIWAXS}}$  becomes moderately more positive as the deposition rate is increased, corresponding with an increase in out-of-plane scattering. By examining Fig. 4(a) at a single deposition rate, we can also observe the variation of scattering anisotropy with substrate temperature. Samples were deposited at a rate near  $8 \text{ \AA s}^{-1}$  for all nine  $T_{\text{sub}}$  studied. The samples deposited at the highest  $T_{\text{sub}}$  have mildly negative or zero values of  $S_{\text{GIWAXS}}$ , indicating a slight tendency for in-plane scattering intensity or completely isotropic glasses. As  $T_{\text{sub}}$  is lowered, the values for  $S_{\text{GIWAXS}}$



**FIG. 4.** The orientational Hermans order parameter  $S_{\text{GIWAXS}}$  vs the actual and effective deposition rate. (a)  $S_{\text{GIWAXS}}$  of the  $q \approx 1.4 \text{ \AA}^{-1}$  peak as a function of the log of the deposition rate for nine substrate temperatures. Error bars given are the standard deviation in calculated  $S_{\text{GIWAXS}}$  over three spots on each sample. Generally,  $S_{\text{GIWAXS}}$  decreases (less out-of-plane scattering intensity) with increasing  $T_{\text{sub}}$  and decreasing deposition rate. (b)  $S_{\text{GIWAXS}}$  vs an effective deposition rate at 293 K calculated by applying the rate-temperature superposition (RTS) principle using the “shift factor” in which raising  $T_{\text{sub}}$  by 17 K during deposition has the equivalent effect on  $S_{\text{GIWAXS}}$  as lowering the deposition rate by a factor of 10. As a guide to the eye, we empirically fit a curve to the data in panel (b); this same curve is horizontally transformed by the shift factor and used in panel (a).

become more positive (increase in out-of-plane scattering), similarly to the case in which the deposition rate is lowered.

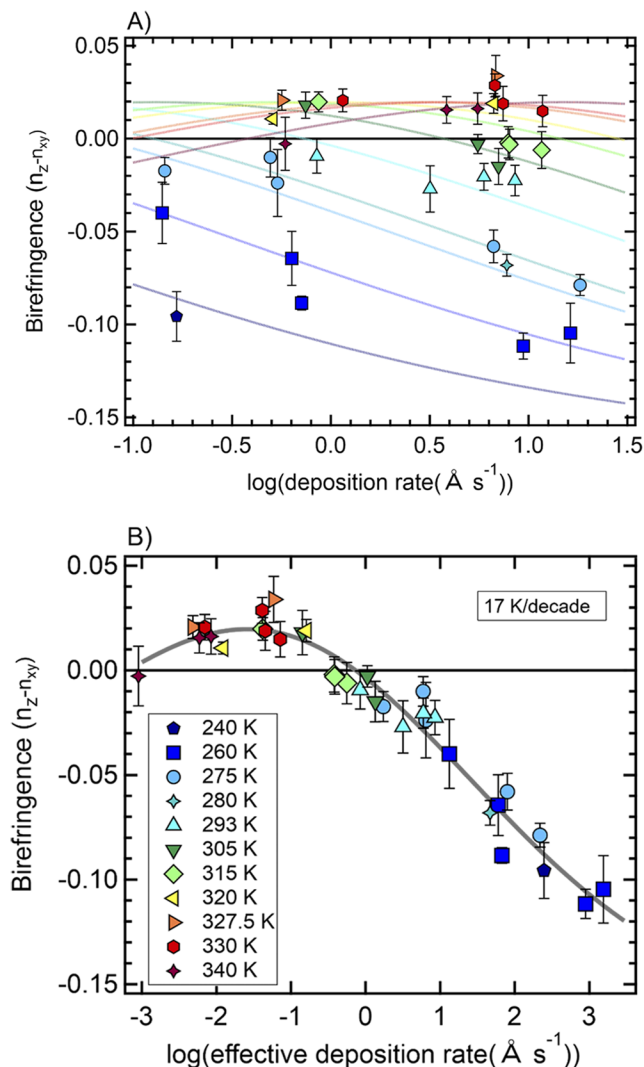
In Fig. 4(b), we examine the relationship between  $T_{\text{sub}}$  and deposition rate further by attempting a quantitative rate-temperature superposition. The scattering anisotropy depends upon both the deposition rate and the substrate temperature, and we combine the two parameters into a single “effective deposition rate” i.e., the rate at which the glass must be deposited at the reference

temperature in order to achieve the specified scattering anisotropy. We choose room temperature (293 K) as the reference temperature, as this is often the temperature at which glasses are prepared for OLEDs on an industrial scale. We test a multitude of “shift factors” to find a smooth collapse of data into a master curve, as illustrated graphically in previous publications.<sup>31,32</sup> For each tested shift factor, we transform the actual deposition rate to an effective deposition rate based upon the  $T_{\text{sub}}$ ; glasses deposited at lower  $T_{\text{sub}}$  will have higher effective rates than actual rates. A shift factor of 17 K per decade results in the successful “master curve” shown in Fig. 4(b). This collapse means that raising  $T_{\text{sub}}$  by 17 K during deposition will prepare a glass with  $S_{\text{GIWAXS}}$  equivalent to one made by depositing 10 times more slowly at the original substrate temperature. We note that at the lowest effective deposition rates,  $S_{\text{GIWAXS}}$  approaches zero (the glass becomes more isotropic) after reaching a minimum. This is consistent with a mechanism proposed for non-liquid crystal molecules, in which  $T_{\text{sub}}$  and rate control not only the rate of equilibration but also the equilibration depth.<sup>32</sup>

We also measured the optical birefringence of the PVD glasses of ABH113. The birefringence is the difference between the out-of-plane and in-plane indices of refraction; a positive birefringence indicates a higher refractive index out-of-the-plane of the film. The birefringence is primarily controlled by the average molecular orientation,<sup>24</sup> with a positive birefringence indicating that the molecular axis with the largest polarizability tends to be vertically oriented in the film. For ABH113, the molecular long axis (along the 9, 10 axis of the anthracene) is expected to have the largest polarizability. Figure 5(a) shows the birefringence of glasses prepared at several  $T_{\text{sub}}$  as a function of the deposition rate. Generally, when deposited at higher rates, the birefringence of the glasses becomes more negative, i.e., the long axes of the ABH113 molecules tend to lie in the plane of the substrate.

Despite the noise in the birefringence data (due to thin samples), a master curve produced by rate-temperature superposition results in a clear trend. Figure 5(b) shows the birefringence as a function of the effective deposition rate at 293 K. For this curve, we used the “shift factor” found for the  $S_{\text{GIWAXS}}$  data (17 K/decade) and found that it superposes the data effectively. Therefore, we determine that all data are consistent with one shift parameter. This differs from other systems that have been previously studied, which show different shift factors for the scattering anisotropy and the optical birefringence; this topic is further explored in the section titled Discussion.

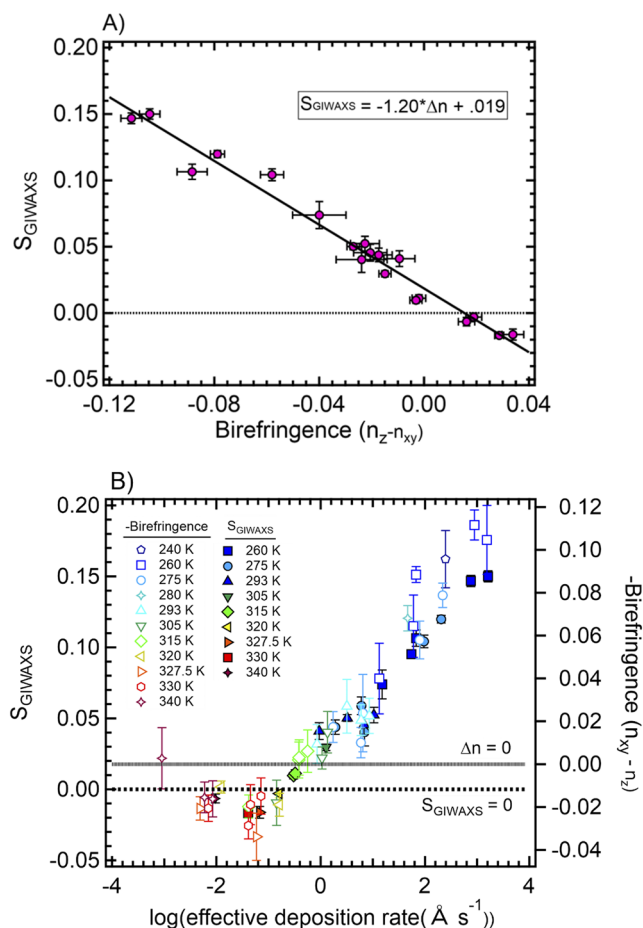
Figures 4 and 5 suggest a strong correlation between anisotropic order in the x-ray scattering and the molecular orientation. We test this directly in Fig. 6(a) by plotting  $S_{\text{GIWAXS}}$  vs the birefringence. The two observables correlate well, with an  $R^2$  for a linear fit of 0.97, indicating that these two types of anisotropy likely share a common origin, which is the anisotropic structure of the liquid surface according to the surface equilibration mechanism. The negative slope of the data in Fig. 6(a) can be rationalized as follows: At the left side of the panel (lowest  $T_{\text{sub}}$  and highest deposition rates), molecules have a strong tendency to lie in the plane of the substrate (as indicated by negative birefringence), which facilitates a tendency toward face-on stacking in the  $z$  direction (which concentrates scattering along the  $z$  axis, leading to a positive value of  $S_{\text{GIWAXS}}$ .) The best-fit line in Fig. 6(a) has a non-zero  $y$ -intercept, that is, when



**FIG. 5.** The birefringence, a measure of molecular orientation, vs the actual and effective deposition rate. (a) Birefringence, the difference in out-of-plane and in-plane refractive index, vs the log of the deposition rate for eleven substrate temperatures. Generally, birefringence becomes more positive with increasing  $T_{\text{sub}}$  and decreasing deposition rate. (b) Birefringence vs an effective deposition rate at 293 K calculated by applying the rate-temperature superposition (RTS) principle using a shift factor of 17 K/decade. The curve fit to the data in panel (b) is also used in panel (a).

the birefringence is equal to zero,  $S_{\text{GIWAXS}}$  is equal to 0.024. While this does not match simple expectations, there is precedent for this mismatch.<sup>30</sup> It is important to emphasize that a glass with a birefringence of zero (or a  $S_{\text{GIWAXS}}$  value of zero) is a necessary, but not sufficient, condition for a truly isotropic sample.

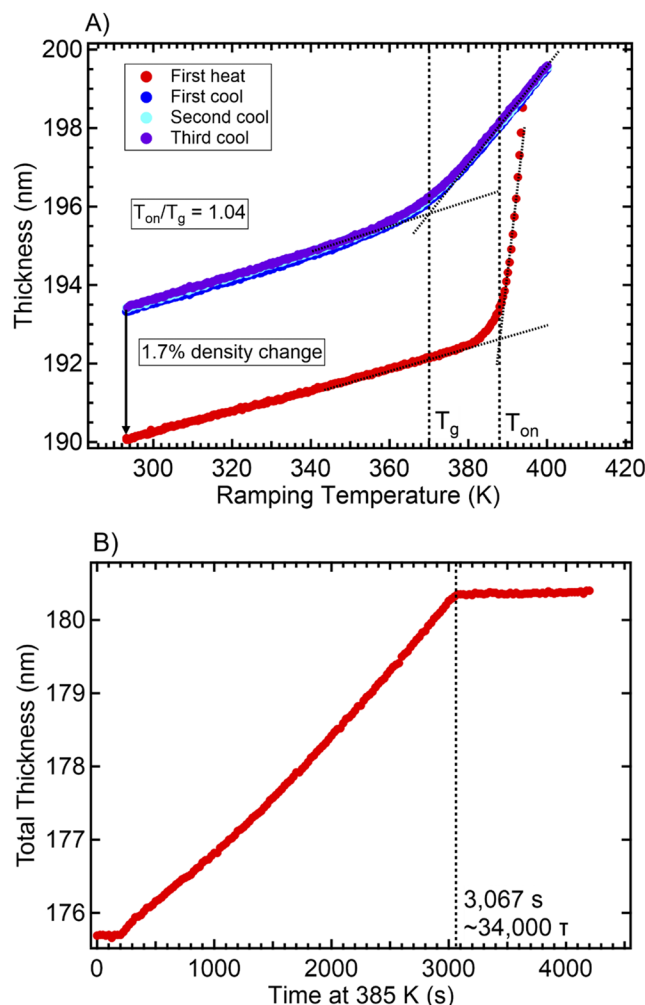
Figure 6(b) shows that the birefringence and  $S_{\text{GIWAXS}}$  values can be combined in a single superposition plot. Within error, the two follow the same functional trend. We note the two different  $y$ -axis positions for the “zero” in Fig. 6(b); this reflects the non-zero  $y$ -intercept in Fig. 6(a).



**FIG. 6.**  $S_{\text{GIWAXS}}$  and birefringence, two measures of anisotropic order, show a strong correlation that allows them to be related by the same rate-temperature superposition shift factor. (a)  $S_{\text{GIWAXS}}$  vs birefringence of the subset of samples measured by both GIWAXS and ellipsometry. A linear fit is shown, with an  $R^2$  of 0.97. (b)  $S_{\text{GIWAXS}}$  and the negative of the birefringence plotted against the log of the effective rate at 293 K shows that the two measures of order follow the same trend. Filled symbols correspond to the x-ray data, while open symbols show the birefringence.

### Thermal stability of vapor-deposited glass

We used ellipsometry measurements during heating to show that the vapor-deposited ABH113 glasses have characteristics of an “ultrastable glass” that include enhanced thermal stability and greater density compared to the liquid-cooled glass. To illustrate this, Fig. 7(a) shows ellipsometry measurements during temperature cycling for a glass that was vapor-deposited at  $6 \text{ Å s}^{-1}$  at  $T_{\text{sub}} = 305 \text{ K}$ . The sample thickness was monitored during heating and subsequent cooling, all at  $1 \text{ K/min}$ . During the first heating experiment, the glass gradually expands as a solid as a result of thermal expansion. This gradual expansion continues even after the ordinary glass transition temperature  $T_g$  ( $370 \text{ K}$ ) is reached. At the onset temperature ( $T_{\text{onset}}$ ) of about  $384 \text{ K}$ , the film thickness rapidly expands due to the



**FIG. 7.** Ellipsometry measurements during sample heating show that a vapor-deposited glass of ABH113 has high thermal stability and high density. (a) Thickness vs temperature of a vapor-deposited glass of ABH113 when heated and cooled at  $1 \text{ K/min}$ . The glass was deposited at  $6 \text{ Å s}^{-1}$  at  $T_{\text{sub}} = 305 \text{ K}$ . The temperature at which the as-deposited glass transforms to the liquid,  $T_{\text{onset}}$ , is equal to  $384 \text{ K}$ ,  $14 \text{ K}$  above the glass transition temperature  $T_g$ , showing enhanced thermal stability. (b) Isothermal transformation of a glass held at  $385 \text{ K}$ ,  $15 \text{ K}$  above  $T_g$ . The glass transforms in  $3067 \text{ s}$ , which is equal to  $34\,000\tau_{\alpha}$ .

transformation of the as-deposited glass into the less dense supercooled liquid. After the transformation into the supercooled liquid was completed, the sample was cooled at  $1 \text{ K/min}$  and vitrified into an ordinary liquid-cooled glass at  $T_g$ . The ordinary glass was then heated and cooled two more times, with good reproducibility.

The as-deposited glass has enhanced thermal stability, as evidenced by the high value of  $T_{\text{onset}}$  in the temperature ramping experiment.  $T_{\text{onset}}$  of the as-deposited glass is measured upon the first heat to be  $384 \text{ K}$ .  $T_g$  is determined from the three cooling experiments to be  $370 \text{ K}$ , which is consistent with  $T_g$  measured by DSC, as shown in Sec. I of the [supplementary material](#).  $T_{\text{onset}}$  for the as-deposited glass of  $384 \text{ K}$  is  $14 \text{ K}$  above  $T_g$ , equal to  $1.04 T_g$ .

$T_g$  and  $T_{\text{onset}}$  are determined from the intersection of the tangents drawn to the thermal expansion of the glass and supercooled liquid. Typical values for “ultrastable glasses” of organic molecules range from  $\sim 1.02 T_g$  to  $1.06 T_g$ ,<sup>36</sup> showing that stability of vapor-deposited ABH113 is comparable to other stable vapor-deposited glasses, including previously studied organic semiconductors.<sup>24</sup>

The temperature ramping experiments in Fig. 7(a) also show that the as-deposited glass is denser than the liquid-cooled glass. At room temperature, the as-deposited glass is 3.3 nm thinner than the liquid-cooled glass—a 1.7% increase in density. This value is similar to the largest density increases measured for PVD glasses of other organic semiconductors<sup>24</sup> and similar molecules.<sup>37,38</sup> Both the higher density and the increased thermal stability of the vapor-deposited glass can be explained by the ability of molecules to find packing arrangements closer to equilibrium during deposition below  $T_g$ , as described further in the section titled Discussion.

To quantitatively evaluate the thermal stability of PVD glasses of ABH113, we performed isothermal annealing experiments above  $T_g$ . Experiments were performed on a glass deposited at  $6 \text{ \AA s}^{-1}$  at  $T_{\text{sub}} = 305 \text{ K}$ . In an isothermal annealing experiment, as shown in Fig. 7(b), the as-deposited glass is held at a single temperature above  $T_g$  and monitored as it transforms to the supercooled liquid. To quantify the thermal stability, the overall time of the transformation is compared to the structural relaxation time of the supercooled liquid at the annealing temperature. For this experiment, we held the as-deposited glass at 385 K, 15 K above  $T_g$ . We estimate the structural relaxation time  $\tau_\alpha$  at 385 K to be 0.09 s using temperature jump experiments, shown in detail in Fig. S4 through S6. When the as-deposited glass is held at 385 K, after a short induction period, the overall measured film thickness slowly begins to increase as the glass transforms into a supercooled liquid. We model the film as a single layer; while the supercooled liquid and as-deposited glass have slightly different optical constants, the overall film thickness is satisfactorily modeled. We assume, consistent with previous literature results, that the glass transforms to a supercooled liquid through a constant-velocity transformation front that initiates at the surface, increasing the overall film thickness in a linear fashion.<sup>39–41</sup> After 3067 s, the film reaches a plateau thickness, indicating that it is completely transformed to the supercooled liquid. Given our estimate of the structural relaxation time  $\tau_\alpha$ , the transformation occurs in  $\sim 34\,000 \tau_\alpha$ , indicating a highly stable glass (see pages 3–5 of the [supplementary material](#) for details.) For comparison, a liquid-cooled glass transforms in  $\sim 1 \tau_\alpha$ , showing that the vapor-deposited glass shown here has enhanced stability.

## DISCUSSION

In many respects, the structure and stability of PVD glasses of ABH113 are similar to previously-studied non-mesogenic organic semiconductors with relevance for OLEDs. The birefringence and  $SG_{\text{IWAXS}}$  as a function of substrate temperature are qualitatively similar to those previously reported for TPD, NPD, and DSA-Ph.<sup>24</sup> In particular, for these three systems and ABH113, glasses deposited at low substrate temperatures have the molecular long axis oriented toward the plane of the substrate, on average,<sup>24,42</sup> while a slight tendency toward vertical orientation is observed for deposition at substrate temperatures close to  $T_g$ . As noted above, the density and thermal stability of PVD glasses of ABH113 are typical of the most

stable glasses prepared to date—and in this way, they are similar to other organic semiconductors that have been studied. The similarity of the PVD glasses of ABH113 to those of other organic semiconductors makes ABH113 a suitable candidate for testing the deposition rate–substrate temperature superposition. We show below that the superposition works well for ABH113, and we expect that it will also apply to many other organic semiconductors.

## Generality of rate-temperature superposition

For some systems, the effects of deposition rate and substrate temperature upon the anisotropic structure of PVD glasses can be related quantitatively using “deposition rate–substrate temperature superposition” or RTS. In PVD, molecules at the surface attempt to equilibrate toward the equilibrium liquid surface structure; this happens relatively rapidly given that mobility at the surface is many orders of magnitude faster than mobility in the bulk.<sup>43</sup> Typically, however, these molecules are kinetically trapped by further deposition before they completely equilibrate. Further equilibration during deposition can be achieved either by depositing at a higher temperature or depositing more slowly. When RTS describes the data, it suggests that adjusting the deposition rate and the substrate temperature are equivalent paths to producing a particular anisotropic structure. Demonstration of RTS is consistent with the surface equilibration mechanism. On a practical level, RTS reduces a two-dimensional parameter space to a single combined variable that controls glass anisotropy. This is important as the anisotropy of vapor-deposited organic semiconductors has been shown to significantly impact device performance through enhancing charge mobility and outcoupling efficiency.<sup>21</sup>

We have previously reported that RTS describes the anisotropic structure of PVD glasses for three systems.<sup>30–32</sup> RTS has been shown to work for itraconazole and posaconazole, model systems of pharmaceutical importance.<sup>31,32</sup> PVD glasses of both of these systems can exhibit high levels of vertical orientation and smectic-like layering. RTS has also been demonstrated for a phenanthroperylene ester that is an organic semiconductor.<sup>30</sup> This phenanthroperylene ester is also a liquid crystal mesogen, forming hexagonal columnar structures both in equilibrium and via PVD.

The demonstration here that the anisotropic structure of PVD glasses of ABH113 follows RTS extends previously published work in several ways. Most importantly, ABH113 is more typical of the molecules used in OLED devices, including deuterium-substitution to increase chemical stability and emitter efficiency. While the phenanthroperylene ester mentioned above is also an organic semiconductor, typical OLED molecules do not have equilibrium liquid crystal phases. One previous study on Alq3, a common OLED emitter, used two deposition rates and found that translational layering order may follow an RTS.<sup>33</sup> This previous work, together with the more comprehensive study of ABH113 presented here, suggests that the RTS principle is broadly useful to predict and control the structure of glasses of industrially relevant molecules used in OLED devices. A second important aspect of the current work is that RTS was observed to work with the same shift factor for both x-ray and birefringence measurements. More complex behavior has been observed for itraconazole and the phenanthroperylene ester, and this complexity is likely associated with the longer range order present in PVD glasses of these molecules.<sup>30,31</sup> A third important aspect



of our work on ABH113 is the wide substrate temperature range over which RTS has been shown to work, extending to substrate temperatures as low as  $0.65 T_g$  for the birefringence measurements. This temperature range is wider than the range tested in previous work and includes room temperature. The demonstration that RTS works at even very low substrate temperature is especially relevant for OLED molecules, which are often deposited at room temperature and often have high glass transition temperatures. Previous work by Yokoyama and co-workers can be interpreted in retrospect as being consistent with RTS, as they found that the molecular orientation of several vapor-deposited OLED molecules depended on the deposition rate when deposited at room temperature ( $\sim 0.70 T_g$ ).<sup>21,23</sup> Finally, we have shown that the ABH113 glasses that follow RTS are also highly stable and higher in density than a liquid-cooled glass. High thermal stability has been shown to extend device lifetimes.<sup>29,44</sup>

The RTS shift factor is a measure of how much the final structure of the glass depends upon both the  $T_{\text{sub}}$  and the rate. The RTS shift factor of 17 K/decade found for ABH113 in this work indicates that, at a single substrate temperature, the molecular packing can be adjusted considerably by changing the deposition rate. This could be important in the manufacture of OLEDs where deposition chambers typically only allow room temperature depositions. Further investigation into the existence of RTS for other relevant OLED parameters, such as thermal stability and density, would further improve the understanding of the effect of deposition rate on the ultimate function of the materials.

### Surface relaxation inferred from rate-temperature superposition

The observation of RTS in PVD glasses of ABH113 is consistent with the surface equilibration mechanism and can be used to gain insight into the surface relaxation process that is responsible for the as-deposited glass structure. From Fig. 6(b), we infer that the surface relaxation time that controls PVD glass structure is on the order of  $10^{2.5}$  s at 293 K (using the effective rate associated with the minimum in this figure and a 1 nm estimate of the relevant surface layer). From this perspective, we see that PVD is useful for preparing glasses with a range of structures because the relevant (surface) relaxation time is not so different from the time required to deposit one molecular layer, even more than 70 K below  $T_g$ . For comparison, the corresponding bulk relaxation time ( $\tau_\alpha$ ) at 370 K is found to be about  $10^4$  s (see the [supplementary material](#)) and by extrapolation would be about  $10^{29}$  s at 293 K. While this extrapolation is certainly rough, it serves to make the point that the equilibrium relaxation times for ABH113 in the bulk are extremely long. Therefore, once a particular anisotropic glass of ABH113 is prepared, it is expected to maintain this structure for extremely long times in the glassy state.

It is useful to compare the surface relaxation process for ABH113 with other systems studied by PVD. In contrast to the previously studied systems, the metrics of the anisotropic structure for ABH113 glasses (birefringence and  $S_{\text{GIWAXS}}$ ) can be described with a common shift factor. The shift factor of 17 K/decade allows us to calculate the activation energy for the molecular rearrangements responsible for anisotropic order in ABH113 glasses, and we find a value of  $\sim 100$  kJ/mol. [For reference, the activation energy for the corresponding bulk relaxation process ( $\tau_\alpha$ ) at  $T_g$  is much

larger, about 900 kJ/mol (see [supplementary material](#)).] For itraconazole and posaconazole, which form layered smectic-like glasses via PVD, the shift factor associated with molecular reorientation is different from the shift factor associated with translational order.<sup>31,32</sup> For these two systems, the activation energy for the process controlling molecular reorientation is about 390 kJ/mol, calculated from a shift factor of  $\sim 5$  K/decade.<sup>32</sup> Recent work by Li *et al.*<sup>45</sup> provides a way to understand the much larger activation energies reported for posaconazole and itraconazole. These authors show that for systems without hydrogen bonding, surface diffusion coefficients are strongly influenced by the depth penetrated by surface molecules. Since posaconazole and itraconazole are nearly vertical at the surface of the equilibrium liquid, they penetrate further from the free surface than is expected for ABH113; the larger penetration depth leads to both slower surface diffusion and a larger activation energy for surface diffusion. Activation energies for the translational layering shift factor for itraconazole are even larger (920 kJ/mol), and this is consistent with the idea that achieving this type of order requires mobility even further away from the free surface. The rather low activation energy for the orientational ordering of ABH113 found in this work suggests that the process takes place at only the very top (1–2 nm) of the film during deposition.<sup>30</sup> The activation energy for ABH113 reported here is similar to the value reported for the surface reorientation process of a phenanthroperylene ester, which has hexagonal columnar liquid crystal phases.<sup>30</sup> The phenanthroperylene ester has a shift factor for both molecular orientation and aromatic core-to-core spacing of 17 K/decade, the same as that reported here for ABH113's molecular reorientation. This suggests that both systems, in contrast to the smectic-like systems of itraconazole and posaconazole (with shift factors of 5 K/decade), have a very mobile surface, and the deposition rate is a powerful variable to control the anisotropic structure.

As a final comment, we note that multiple surface equilibration processes may be relevant for PVD glasses.<sup>31</sup> For example, the surface equilibration that gives rise to anisotropic structures in PVD glasses need not be surface diffusion. These two processes may be related, consistent with the reported correlation between glass stability and surface diffusion coefficients for several molecular glasses.<sup>46</sup> On the other hand, Samanta *et al.*<sup>47</sup> showed that stable glasses can be formed for some molecules even when surface diffusion is negligibly slow. As a second example, we do not know for ABH113 that the surface equilibration process that leads to glass stability is the same as the one that leads to the anisotropic structure. From Fig. 6(b), we see that deposition at  $10^{-3}$  Å/s at 293 K should produce an isotropic thin film. One might infer that this material should be the equilibrium supercooled liquid. One could use density and enthalpy measurements to check this interpretation, but until such experiments are performed, we should be careful not to assume that this is the case.

### CONCLUSIONS

We have shown that the anisotropic structure of vapor-deposited glasses of an organic semiconductor is consistent with the deposition rate–substrate temperature superposition principle. Over a wide range of substrate temperature, from  $0.65$ – $0.92 T_g$ , increasing the substrate temperature has the same effect on the glass structure as decreasing the deposition rate. Notably, these conditions include room temperature (293 K), and, thus, our work

enables structure manipulation via deposition rate in vacuum depositors used industrially. The existence of a single shift factor that describes RTS for both x-ray and optical birefringence measurements implies a particularly simple formation route, consistent with the surface equilibration mechanism. Glasses of ABH113 also show enhanced thermal stability and density. Thus, for this typical OLED molecule, glass packing can be efficiently manipulated over a large range of structures through predictable changes in either substrate temperature or deposition rate while maintaining the tight packing associated with long-lived and energy-efficient devices.

## SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for DSC and  $T_g$  determination of ABH113, x-ray order parameter fitting, and relaxation time determination by ellipsometry.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## REFERENCES

- C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.* **51**(12), 913–915 (1987).
- J.-H. Lee, C.-H. Chen, P.-H. Lee, H.-Y. Lin, M.-k. Leung, T.-L. Chiu, and C.-F. Lin, *J. Mater. Chem. C* **7**(20), 5874–5888 (2019).
- Y. Huang, E.-L. Hsiang, M.-Y. Deng, and S.-T. Wu, *Light: Sci. Appl.* **9**(1), 105 (2020).
- S. Wang, H. Zhang, B. Zhang, Z. Xie, and W.-Y. Wong, *Mater. Sci. Eng., R* **140**, 100547 (2020).
- PRNewswire Research and Markets “The Worldwide OLED Industry is Expected to Reach \$72.8 Billion by 2026 at a CAGR of 13.6% from 2021”. (April 7th, 2021); available at <https://www.prnewswire.com/news-releases/the-worldwide-oled-industry-is-expected-to-reach-72-8-billion-by-2026-at-a-cagr-of-13-6-from-2021-301264145.html>.
- C. Murawski and M. C. Gather, *Adv. Opt. Mater.* **9**, 2100269 (2021).
- Y. Shirota and H. Kageyama, *Handbook of Organic Materials for Optical and (Opto)Electronic Devices: Properties and Applications* (Woodhead Publishing, 2013), pp. 3–82.
- M.-H. Ho, B. Balaganesan, and C. H. F. Chen, *Isr. J. Chem.* **52**(6), 484–495 (2012).
- M. Pope, H. P. Kallmann, and P. Magnante, *J. Chem. Phys.* **38**(8), 2042–2043 (1963).
- J. Huang, J.-H. Su, and H. Tian, *J. Mater. Chem.* **22**(22), 10977–10989 (2012).
- M. Aydemir, G. Haykir, A. Battal, V. Jankus, S. K. Sugunan, F. B. Dias, H. Al-Attar, F. Türksoy, M. Tavasli, and A. P. Monkman, *Org. Electron.* **30**(C), 149–157 (2016).
- J. Cho, S. H. Kim, J. H. Kim, S. Park, and S. Y. Park, *J. Mater. Chem.* **22**(1), 123–129 (2012).
- H. Park, J. Lee, I. Kang, H. Y. Chu, J.-I. Lee, S.-K. Kwon, and Y.-H. Kim, *J. Mater. Chem.* **22**(6), 2695–2700 (2012).
- M.-T. Lee, H.-H. Chen, C.-H. Liao, C.-H. Tsai, and C. H. Chen, *Appl. Phys. Lett.* **85**(15), 3301–3303 (2004).
- M.-T. Lee, C.-H. Liao, C.-H. Tsai, and C. H. Chen, *Adv. Mater.* **17**(20), 2493–2497 (2005).
- H. Tsuji, C. Mitsui, and E. Nakamura, *Chem. Commun.* **50**(94), 14870–14872 (2014).
- A. Danos, R. W. MacQueen, Y. Y. Cheng, M. Dvořák, T. A. Darwish, D. R. McCamey, and T. W. Schmidt, *J. Phys. Chem. Lett.* **6**(15), 3061–3066 (2015).
- Y. Lee, E. J. Jang, H. Seo, and D. Y. Chung, U.S. patent 11038112 (June 15th, 2021).
- P. Wang, F.-F. Wang, Y. Chen, Q. Niu, L. Lu, H.-M. Wang, X.-C. Gao, B. Wei, H.-W. Wu, X. Cai, and D.-C. Zou, *J. Mater. Chem. C* **1**(32), 4821–4825 (2013).
- C. C. Tong and K. C. Hwang, *J. Phys. Chem. C* **111**(8), 3490–3494 (2007).
- D. Yokoyama, *J. Mater. Chem.* **21**, 19187–19202 (2011).
- J. Frischeisen, D. Yokoyama, C. Adachi, and W. Brütting, *Appl. Phys. Lett.* **96**(7), 073302 (2010).
- M. Shibata, Y. Sakai, and D. Yokoyama, *J. Mater. Chem. C* **3**(42), 11178–11191 (2015).
- S. S. Dalal, D. M. Walters, I. Lyubimov, J. J. de Pablo, and M. D. Ediger, *Proc. Natl. Acad. Sci. U. S. A.* **112**(14), 4227 (2015).
- S. F. Swallen, K. L. Kearns, M. K. Mapes, Y. S. Kim, R. J. McMahon, M. D. Ediger, T. Wu, L. Yu, and S. Satija, *Science* **315**(5810), 353 (2007).
- T. D. Schmidt, T. Lampe, D. Sylvainson M. R. P. I. Djurovich, M. E. Thompson, and W. Brütting, *Phys. Rev. Appl.* **8**(3), 037001 (2017).
- C. Mayr and W. Brütting, *Chem. Mater.* **27**(8), 2759–2762 (2015).
- L. Berthier, P. Charbonneau, E. Flenner, and F. Zamponi, *Phys. Rev. Lett.* **119**(18), 188002 (2017).
- J. Ràfols-Ribé, P.-A. Will, C. Hänisch, M. Gonzalez-Silveira, S. Lenk, J. Rodríguez-Viejo, and S. Reineke, *Sci. Adv.* **4**(5), eaar8332 (2018).
- C. Bishop, Z. Chen, M. F. Toney, H. Bock, L. Yu, and M. D. Ediger, *J. Phys. Chem. B* **125**(10), 2761–2770 (2021).
- C. Bishop, A. Gujral, M. F. Toney, L. Yu, and M. D. Ediger, *J. Phys. Chem. Lett.* **10**(13), 3536–3542 (2019).
- C. Bishop, Y. Li, M. F. Toney, L. Yu, and M. D. Ediger, *J. Phys. Chem. B* **124**(12), 2505–2513 (2020).
- K. Bagchi, N. E. Jackson, A. Gujral, C. Huang, M. F. Toney, L. Yu, J. J. de Pablo, and M. D. Ediger, *J. Phys. Chem. Lett.* **10**(2), 164–170 (2019).
- J. J. Hermans, P. H. Hermans, D. Vermaas, and A. Weidinger, *Recl. Trav. Chim. Pays-Bas* **65**(6), 427–447 (1946).
- A. Gujral, K. A. O’Hara, M. F. Toney, M. L. Chabinyc, and M. D. Ediger, *Chem. Mater.* **27**(9), 3341–3348 (2015).
- K. R. Whitaker, M. Tylinski, M. Ahrenberg, C. Schick, and M. D. Ediger, *J. Chem. Phys.* **143**(8), 084511 (2015).
- S. S. Dalal, A. Sepúlveda, G. K. Pribil, Z. Fakhraai, and M. D. Ediger, *J. Chem. Phys.* **136**(20), 204501 (2012).
- T. Liu, K. Cheng, E. Salami-Ranjbaran, F. Gao, C. Li, X. Tong, Y.-C. Lin, Y. Zhang, W. Zhang, L. Klinge, P. J. Walsh, and Z. Fakhraai, *J. Chem. Phys.* **143**(8), 084506 (2015).
- S. F. Swallen, K. Windsor, R. J. McMahon, M. D. Ediger, and T. E. Mates, *J. Phys. Chem. B* **114**(8), 2635–2643 (2010).
- E. Flenner, L. Berthier, P. Charbonneau, and C. J. Fullerton, *Phys. Rev. Lett.* **123**(17), 175501 (2019).

- <sup>41</sup>C. Rodríguez-Tinoco, M. Gonzalez-Silveira, J. Ràfols-Ribé, A. Vila-Costa, J. C. Martinez-Garcia, and J. Rodríguez-Viejo, *Phys. Rev. Lett.* **123**(15), 155501 (2019).
- <sup>42</sup>K. Bagchi, A. Gujral, M. F. Toney, and M. D. Ediger, *Soft Matter* **15**(38), 7590–7595 (2019).
- <sup>43</sup>L. Yu, *Adv. Drug Delivery Rev.* **100**, 3–9 (2016).
- <sup>44</sup>Y. Esaki, T. Komino, T. Matsushima, and C. Adachi, *J. Phys. Chem. Lett.* **8**(23), 5891–5897 (2017).
- <sup>45</sup>Y. Li, W. Zhang, C. Bishop, C. Huang, M. D. Ediger, and L. Yu, *Soft Matter* **16**(21), 5062–5070 (2020).
- <sup>46</sup>Y. Chen, M. Zhu, A. Laventure, O. Lebel, M. D. Ediger, and L. Yu, *J. Phys. Chem. B* **121**(29), 7221–7227 (2017).
- <sup>47</sup>S. Samanta, G. Huang, G. Gao, Y. Zhang, A. Zhang, S. Wolf, C. N. Woods, Y. Jin, P. J. Walsh, and Z. Fakhraai, *J. Phys. Chem. B* **123**(18), 4108–4117 (2019).